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Potential of biochar soil amendments to reduce N leaching in boreal field conditions estimated using the resin bag method

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ABSTRACT

Addition of biochar to soil has been shown to reduce nitrogen (N) leaching in pot experiments, but direct field measurements are scarce, and data is lacking especially from colder, boreal conditions. We studied the effect of soil organic amendments on nitrate (NO_3^-) and ammonium (NH_4^+) leaching using the resin bag method, by placing the bags containing ion-exchange resins under the plough layer. We compared N leaching under five different treatments at the Päästösäästö project site (Soilfood Oy) in Parainen, south-western Finland: non-fertilized control, fertilized control, and three different organic amendments: spruce biochar, willow biochar and nutrient fiber. During the 2017 growing season, resin bags were changed monthly between the end of May and beginning of September, extracted with 1 M NaCl, and analyzed for inorganic N. The daily leaching rate of NO_3^- was greatest at the beginning of the growing season, right after fertilization. Ammonium leaching was generally lower, and independent of the time since fertilization. The spruce biochar reduced cumulative NO_3^- leaching by 68% compared to the fertilized control. The NH_4^+ leaching in the organic amendment treatments did not statistically significantly differ from the fertilized control in pairwise comparisons. In October 2017, after harvesting, the resin bags were placed under soil columns again, and left in the soil over winter to accumulate N leached during the plant-free period. Cumulative NO_3^- leaching during winter was consistent with the corresponding summer results, and average leaching decreased in the order: willow biochar > fertilized control > nutrient fiber > non-fertilized control > spruce biochar. Thus, we show here, for the first time in a field study from boreal conditions that spruce biochar soil application decreased nitrate leaching, while increasing its retention in the surface layer of the biochar-amended soil.

1. Introduction

Leaching of nitrogen (N) from agricultural fields is harmful, because it can cause eutrophication of waterways, and become transformed into a potent greenhouse gas N_2O in the denitrification process (Galloway et al., 2008). Especially nitrate (NO_3^-) is susceptible to leaching, since it is not adsorbed onto soil surfaces (Jaakkola, 1984). Biochars have been suggested as means to mitigate N-losses from agriculture, by retaining N from added fertilizers (González et al., 2015; Zheng et al., 2013), or from co-composted N-rich organic waste (Kammann et al., 2015). Reduced N leaching from biochar amended soils has been documented only in field experiments from warmer climates (Angst et al., 2014; Borchard et al., 2019; Güereña et al., 2013; Haider et al., 2017; Mia et al., 2017). Whether such an environmental benefit of biochar soil amendments is available also in cool boreal climates remains unknown. Biochars can reduce NH_4^+ leaching by increasing the cation exchange capacity of soils (Liang et al., 2006; Gai et al., 2014). Biochars may also increase soil water holding capacity (Karhu et al., 2011; Novak et al., 2012), due to their large surface area and high porosity, thereby reducing soil water percolation and the N contained in it (Glaser et al., 2002; Yoo et al., 2014). Since precipitation will increase with climate warming in the already humid boreal climate (IPCC, 2013), there is a risk for increased N leaching (Jabloun et al., 2015). Therefore, there is a pressing need for field studies on the effects on biochar and other soil amendments on N leaching in boreal conditions.

The effects of biochar on soil N dynamics may change with time

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(Borchard et al., 2019). Even though biochars can persist in soils for several thousand years (Kuzyakov et al., 2014), some studies reported that the mean residence times of biochars were much lower than expected (de la Rosa et al., 2018). As a result, the positive effects of biochar can fade away even after few growing seasons (Cornelissen et al., 2018). On the other hand, field aging can increase surface oxidation of biochar particles by increasing oxygen containing functional groups, particularly carboxylic and phenolic functional groups. Development of such functional groups increases the negative surface charge density and can increase adsorption of NH_4^+ (Mia et al., 2017). Similarly, field aging of biochar particles can help in the formation of organic coating due to the development of organo-mineral complexes, which can promote the retention of NO_3^- (Hagemann et al., 2017; Joseph et al., 2018). Cheng et al. (2008) reported that the surface oxidation of biochar particles positively correlated with mean annual temperature, and thus higher oxidation can be expected in warmer climates. It remains uncertain whether such changes in biochar particles could be expected in cooler boreal region after a few years of field aging. Moreover, in a meta-analysis compiling 1125 observations from 109 studies, it was reported that biochar increased crop yields in warmer tropical regions, but had no effect in cooler temperate regions (Jeffery et al., 2017). As higher temperature favors increased N plant uptake by the growing plants and thus reduces N leaching (Ineson et al., 1998), the effect of biochar on crop yield or plant N uptake and hence N leaching could be limited in cooler boreal climates.

The addition of biochar or other soil amendments generally increases soil microbial biomass (Lehmann et al., 2011). Such increased microbial biomass can entrap the added fertilizer N into their biomass, causing N immobilization (Bruun et al., 2012; Tammeorg et al., 2012), which helps to prevent N leaching (Xu et al., 2016). In a meta- analysis of a total of 550 laboratory incubation, pot and field scale studies, Zhou et al. (2017) reported that biochar increased MBC by 26% and MBN by 21%. However, when comparing the different studies, they found that biochar on average enhanced MBN in incubation studies by 42%, but had no effect in pot and field studies. They stressed the need for exploring microbial responses to biochar additions in long-term field experiments. Such immobilized N in microbial biomass can be re-mineralized later (Aoyama and Nozawa, 1991), especially during freeze-thaw events (Gao et al., 2017), which makes it susceptible for leaching again in field conditions. In seasonally snow-covered regions, climate warming will decrease snow-cover and the duration of snowpack, resulting in less insulation of the soil, and increasing occurrence of freeze-thaw cycles during the winter. These freeze-thaw effects can change N cycling, and increase N leaching losses (Watanabe et al., 2019), which highlights the need for N leaching studies from boreal climates.

Generally, NO_3^- leaching rates are known to increase with increasing precipitation in Nordic conditions (Jabloun et al., 2015). Climate change leads to warmer winters and increasing precipitation especially in wintertime, increasing N leaching from agricultural fields to the Baltic Sea (Huttunen et al., 2015). According to worst-case scenarios, N loads are projected to increase by 36% by the end of the century (Pihlainen et al., 2020). New methods for reducing nutrient leaching from agriculture are urgently needed, since the warmer and wetter winters have already been shown to counteract the traditional mitigation measures, so that Finland will not achieve the nutrient reduction targets set by HELCOM for the Baltic sea region by 2021 (Räike et al., 2020). We tested whether soil application of biochar can reduce N leaching during the 2017 growing season, and during autumn and winter 2017–2018. October and December 2017 happened to be exceptionally rainy compared to long-term average (FMI, 2020). This makes our study a unique field trial for investigating the potential of biochar soil amendments in mitigating N leaching under future warmer and wetter conditions.

We hypothesized that 1) biochars as organic amendments could reduce NO_3^- and NH_4^+ leaching below the plough layer by retaining them in the surface soils via different physico-chemical mechanisms; either physically within biochar pore structures, or via cation exchange on biochar surfaces; 2) Nutrient fiber as organic amendment could reduce N leaching through biological interactions, by increasing microbial biomass that could retain N through immobilization; 3) Since biochars have high C:N ratios, and may increase microbial biomass in soil, they could also increase retention of N through microbial immobilization.

2. Material and Methods

2.1. Field experiment

We studied the effect of biochars and nutrient fiber on NH_4^+ and NO_3^- leaching at the Päästösäästö field site (Soilfood Oy) in Parainen, south-western Finland (60°17'44"N, 22°23'35"E). The field site was established in 2016 on a clay soil (54% clay, 34% silt, 12% sand). The soil classification according to WRB was Vertic Endogleyic Stagnic Cambisol (clayic) (WRB, 2007). The field has a subsurface drainage system in the depth of 100–120 cm. The drainage system at the site together with the farming practices applied makes the study site a representative clayey soil field in humid boreal climate. The management of agricultural soils in this region of south-western Finland is important for the water quality of the Baltic Sea (Pihlainen et al., 2020), specifically for the Archipelago Sea area, where they drain (Huttunen et al., 2015). The experimental treatments were established in a randomized complete block design with three replicate blocks, each treatment taking up one 5 m × 16 m plot in each block. The organic amendments were harrowed into the top 10 cm soil layer on 13–14 September 2016 as a one time application. The average soil organic carbon (SOC) concentration in the 0–20 cm layer before applying the treatments was 2.4% and the organic matter content estimated by loss on ignition was 7.1%. Soil properties in 2016 prior to starting the experiment, and one year after adding the organic amendments, i.e. in autumn 2017, are presented in Table 1. Soil pH and EC were determined from 1:5 (w/w) soil to water ratio using standard electrodes (Vuorinen and Mäkitie, 1955). Soil cation exchange capacity was determined with the barium chloride method (ISO 11260:1994; Rhoades, 1983). Total soil C and N were determined by the dry combustion method, and soil organic matter content was determined by the loss on ignition method (Nelson and Sommers, 1983). The five treatments selected for the N-leaching measurements of this study in May 2017 were: non-fertilized control, N-fertilized control (80 kg N ha^{-1}), and three selected treatments with organic amendments: willow biochar (Soilfood Oy), spruce biochar (Soilfood Oy) and ligneous fiber (a commercial product by Soilfood Oy, hereafter called "nutrient fiber" in the text). The pyrolysis temperature of both biochars was 450 °C. All treatments with organic amendments received the same level of mineral N-fertilization (80 kg N ha^{-1} per year) as N-P-K fertilizer (Yara Mila 3, 23–3–8), i.e. the rates of P-, and K-fertilization were 10.4 kg P ha^{-1} per year and 27.8 kg K ha^{-1} per year. The fertilizer had 23% of total N, in the form of NO_3-N (10% of weight) and NH_4^+-N (13% of weight). The general properties of these organic amendments, and BET (Brunauer-Emmett--Teller) surface areas of the biochars, are presented in Table 2. Wheat (*Triticum aestivum*) was grown on the plots in the 2017 growing season, and the soil was left bare for the duration of the winter.

2.2. Resin bag measurements

The circular, water permeable bags containing ion-exchange resins: 6 g of Amberlite, IR 120 (Na^+- ion exchanger resin), and 6 g Dowex 1 × 8 (Cl^- -ion exchanger resin) were placed under the plough layer for N leaching measurements. We used 10 cm diameter PVC tubes to core ca. 20 cm deep intact soil columns, and lift these up using the PVC tube. The resin bags were then placed under the intact soil columns, one resin bag per plot (n = 3 per treatment) and the intact soil column was placed back on top of the resin bag using the PVC tube. The NO_3^- and NH_4^+ accumulated on the resins were used as a measure of mineral N leached over the period the resins remained in the field.

Table 1
Soil chemical properties prior to application of organic amendments in the autumn 2016 (starting point of the whole experimental field, n = 45), and in the autumn 2017 presented separately for the five experimental treatments included in this study (n = 3 per treatment) (average ± S.E).

Treatments	Organic matter (%)	C (%)	N (%)	C:N	Electrical conductivity (mS cm^{-1})	pH (H_2O)	CEC (cmol (+) kg^{-1})
Starting point	7.1 ± 0.08	2.4 ± 0.03	0.3 ± 0.003	8.8 ± 0.05	15 ± 0.46	6.4 ± 0.03	18.2 ± 0.31
Control	7.34 ± 0.02 a	2.58 ± 0.08 a	0.3 ± 001 a	8.6 ± 0.25 a	11.4 ± 1.44 ab	6.47 ± 0.21 a	20.17 ± 2.07 a
Fertilized control	6.90 ± 0.38 a	2.60 ± 0.18 a	0.29 ± 0.01 a	9 ± 0.38 ab	10.38 ± 1.19 a	6.46 ± 0.17 a	19.00 ± 0.80 a
Nutrient fiber	7.36 ± 0.54 a	2.53 ± 0.21 a	0.29 ± 0.02 a	8.54 ± 0.16 a	12.07 ± 0.44 ab	6.48 ± 0.13 a	18.77 ± 0.40 a
Willow biochar	7.50 ± 0.34 a	3.07 ± 0.32 ab	0.29 ± 0.01 a	10.4 ± 0.58 bc	15.55 ± 1.00 b	6.94 ± 0.08 a	22.83 ± 1.75 a
Spruce biochar	7.66 ± 0.58 a	3.32 ± 0.26 b	0.28 ± 0.01 a	11.57 ± 0.5 c	11.18 ± 1.39 ab	6.59 ± 0.05 a	20.15 ± 0.24 a

Different letters signify statistically significant differences in soil properties between treatments in 2017 (one-way ANOVA followed by Tukey's test).

Table 2
Properties and application rates of the organic amendments in 2016.

Organic amendments	Applied amount (t ha^{-1})	Total C input (kg ha^{-1})	Total N input (kg ha^{-1})	CN ratio	Water soluble N (kg ha^{-1})	pH (1:5 H_2O)	EC (mSm^{-1})	BET surface area (m^{2}g^{-1})[a]
Nutrient fiber	24	3250	90	36	0.27	8.9	17	–
Willow biochar	33	18016	373	48	0.31	9.8	30	1.3 ± 0.005
Spruce biochar	21	18999	86	221	0.10	8.3	9.4	328.2 ± 2.1

[a] measured by N_2 adsorption using Micromeritics 3Flex.

In spring 2017, resin bags were placed into the soil on 22 May, 5 days after fertilization and sowing of wheat (*Triticum aestivum*). Thereafter, the resin bags were replaced approximately monthly between the end of June and beginning of September. The exact periods for N leaching measurements during the growing season were 22 May to19 June 2017, 19 June to 28 July 2017, and 28 July to 5 September 2017. Cumulative N leaching over the growing season was calculated by summing up the amounts of NO_3^- and NH_4^+ accumulated on the resins during these three collection periods. There were on average two wheat plants growing inside each PVC tube. After collecting the resin bags on 5 September 2017 and removing the PVC tubes, wheat grown on the plots was harvested on 6 September 2017, and later in October, the soil was disc harrowed to approximately 5–10 cm. On 27 October 2017, the PVC tubes that had been taken out of the soil prior to harvest, were placed again on the same spots, and new resin bags were placed under the soil cores to collect mineral N over the plant-free winter period until 6 May 2018. The resin bags were not replaced monthly during winter because of snow and frozen soil.

After removing the resin bags from the soil, the bags were cleaned with Milli-Q water, and shipped cooled to the Institute of Forest Ecology and Soil in Vienna for analysis. The resin bags were extracted within 5 days from collecting from the soil. The resin bags were extracted twice with 100 mL of 1 M NaCl (shaken for 30 min on an orbital shaker, 169 revolutions per minute), and filtered into a plastic bottle through Sartorius Folded Filters (Qual., Grade: 3 hw). Two blank filters were always included in the extraction and analysis of each batch. The extracts were analyzed for NH_4^+ and NO_3^- concentrations using the method described in Hood-Nowotny et al. (2010). Samples were analyzed at 660 nm (NH_4^+) and 540 nm (NO_3^-) wavelengths using a microplate spectrophotometer (μQuant, BioTek Instruments, Bad Friedrichshall, Germany). Our approach allowed the calculation of N leaching rates per m^2 (area of the round resin bags was 0.007854 m^2) and per day.

2.3. Measurements of soil microbial biomass and extractable mineral N

In May 2018, 10 soil core samples (core diameter 2.7 cm, sampling depth 0–10 cm) were taken from each plot and pooled to form a composite sample. The fresh soil was sieved to 4 mm and analyzed for soil mineral N and microbial biomass. For soil mineral N, about 5 g of fresh sieved soil was extracted with 25 mL 1 M KCl, shaken for 30 min in a mechanical shaker, filtered through Sartorius™ Grade 3-HW folded filters (diameter 150 mm), and stored frozen (− 20 °C) before measuring with an automated flow analyzer Lachat QuikChem 8000 (Zellweger Analytics, Milwaukee, Wisconsin, USA). Microbial biomass C (MBC) and N (MBN) were determined using the chloroform fumigation extraction (CFE) method (Vance et al., 1987) with the following modifications. About 8 g of fresh sieved soil was fumigated with chloroform inside a desiccator for 24 h in the dark, and then extracted with 40 mL of 0.05 M K_2SO_4. A control for the same sample without fumigation was also extracted in the same way. The extracts were analyzed for dissolved organic carbon (DOC) and total dissolved nitrogen (TN) using a Schimadzu TOC-V cph/cpn analyzer (Kyoto, Japan). The MBC and MBN were calculated as the difference in DOC and TN contents in chloroform fumigated and control samples, respectively.

2.4. Statistical analysis

All statistical analyses were conducted using IBM SPSS Statistics 25. All data were checked for homogeneity of variances (Levene's test), and normality (Shapiro-Wilk test). The daily N leaching rates, and the cumulative N leaching data, violated the assumption of homogeneity of variances, and hence were ln-transformed prior to analysis of variance (ANOVA). For studying the seasonality of N leaching rates, repeated measures ANOVA was used. Daily leaching rates of NH_4^+ and NO_3^- (separately for each measurement period), cumulative growing season and winter N leaching data (separately), soil extractable NO_3^-, NH_4^+ concentrations and microbial biomass N and C were analyzed using one-way blocked ANOVA. In statistical analysis, the fertilized control, with the same added N-fertilizer level (80 kg ha^{-1}) as in the treatments that also received organic amendments, was chosen as the control treatment, against which all the other treatments were compared to. Thus, following ANOVA, for each parameter, the means of the organic amendments were compared to that of the fertilized control using Dunnett's two-sided *t*-test.

3. Results

3.1. Nitrogen leaching during the growing season

Over the growing season 2017, the average daily NH_4^+ leaching rate did not statistically significantly depend on the period of N leaching measurements (22 May to 19 June, 19 June to 28 July, or 28 July to 5 September 2017) ($F = 3.29$, $p = 0.058$), and there was no significant time × treatment interaction ($F = 0.64$, $p = 0.73$) (Fig. 1a). The NO_3^- leaching rate was greater in the spring right after fertilization, and clearly decreased with time (significant main effect of time, $F = 38.82$, $p < 0.001$) (Fig. 1b). This seasonal development was similar in all treatments (no significant time × treatment interaction, $F = 0.79$,

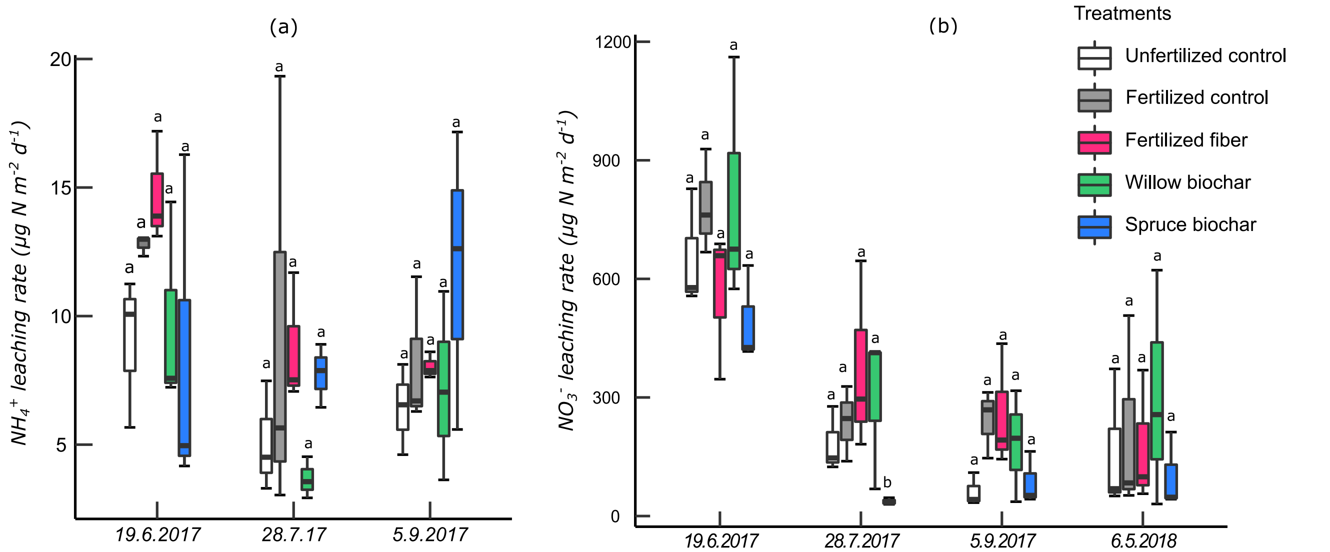

Fig. 1. Rate of a) NH_4^+ and b) NO_3^- leaching into resin bags during the three collection periods within the growing season: 22 May to 19 June 2017, 19 June to 28 July 2017 and 28 July to 5 September 2017. For NO_3^- leaching, data are given also for the winter period 27 October 2017 to 6 May 2018 (x-axis labels correspond to the last days of each collection period). Treatments that differ statistically significantly ($p < 0.05$) from the fertilized control are marked with different lower case letters.

$p = 0.65$). When a statistical test was carried out separately for each leaching measurement period, the spruce biochar treatment significantly reduced the NO_3^- leaching rate compared to the fertilized control treatment during the second N leaching measurement (19 June to 28 July, Fig. 1b), whereas no effects were observed on NH_4^+ and NO_3^- leaching rates during other measurement periods.

During the growing season 22 May to 5 September 2017, the cumulative amount of NH_4^+ (mg N m^{-2}) leached into the resin bags (Fig. 2a) differed almost significantly between treatments ($F = 3.595$, $p = 0.058$), but the block did not have a significant effect ($F = 0.901$, $p = 0.444$). For growing season cumulative NO_3^- leaching (Fig. 2b), the treatment effect was nearly statistically significant ($F = 3.514$, $p = 0.061$), and there were no differences between blocks ($F = 1.155$. $p = 0.362$). In pairwise comparisons, only the cumulative NO_3^- amount leached in the spruce biochar treatment differed statistically significantly from the fertilized control (Dunnett's *t*-test, $p = 0.048$). The difference in the average cumulative NO_3^- leaching between the spruce biochar treatment and the fertilized control treatment was of significant magnitude: spruce biochar reduced NO_3^- leaching during the growing season by 68% compared to the fertilized control treatment (Fig. 2b). The growing season 2017 was drier than the long-term average (Fig. 3a).

3.2. Nitrogen leaching during the winter

In the winter data, the amounts of NH_4^+ accumulated in the resin bags were small, and due to relatively high background NH_4^+ levels in the blank resin bags at this extraction time, the NH_4^+ values were sometimes negative after deduction of blank values. There were no differences between treatment averages (data not shown).

The wintertime cumulative NO_3^- leaching was of the same magnitude as the leaching during the growing season. When averaged across all plots and all treatments, the NO_3^- leaching during the growing season was approximately 48% of the total cumulative (annual) NO_3^- leaching. Within each treatment, variability was higher in the winter than during the growing season, and differences between treatments were not statistically significant ($F = 0.886$, $p = 0.500$) (Fig. 2c). The high variability within treatment was due to differences between blocks ($F = 11.901$, $p = 0.008$): block 1 had much higher cumulative leaching of NO_3^- compared to other blocks (Fig. 2d). On average, the spruce biochar treatment had 52% lower NO_3^- leaching during the winter than the fertilized control treatment, so the difference was less clear than during the summer. Monthly precipitation in October 2017 was 38% higher, and in December 101% higher, compared to the long-term (1981–2010) average (Fig. 3a). The monthly mean temperatures of November and December 2017 were two to three degrees warmer than the long-term average (Fig. 3b). Despite the larger variability, the winter cumulative average NO_3^- leaching of different treatments decreased in the same order as in summer: willow biochar > fertilized control > fertilized fiber > unfertilized control > spruce biochar. The Pearson correlation between summer and winter treatment averages was $r = 0.82$ ($n = 5$, $p = 0.088$).

3.3. Soil extractable mineral N, microbial biomass, grain yield and N content

The treatment effect on NO_3^- concentrations in the uppermost 10 cm was significant overall, while there were no differences between blocks (Table 3). The concentration of extractable NO_3^- in soil was significantly higher in the spruce biochar treatment compared to fertilized control treatment in spring 2018 (Dunnett's *t*-test, $p = 0.005$) (Fig. 4a). We also measured higher NH_4^+ concentrations from the surface soils of the willow biochar treatment compared to other treatments in spring 2018, but this difference was not statistically significant due to high variability within the willow biochar treatment (Fig. 4b, Table 3). There were no statistically significant differences between treatments in microbial biomass C (Fig. 4c) or N (Fig. 4d; Table 3). The differences in N leaching or soil N retention did not affect grain yields nor their N contents (Table 4); only the unfertilized control had a lower grain yield compared to the fertilized control in 2017.

4. Discussion

4.1. Comparison of summer and winter N leaching

Our NO_3^- leaching results over the summer and winter periods were consistent; the average cumulative N leaching of the different treatments always decreased in the same order. These consistent results indicate that the method provided reproducible results, despite the rather large variability in the field. The NO_3^- leaching pattern in the growing season in summer suggests that irrespective of the treatments, the greatest N leaching occurred right after fertilization, when plant roots were not fully developed to take up NO_3^-. However, in the second

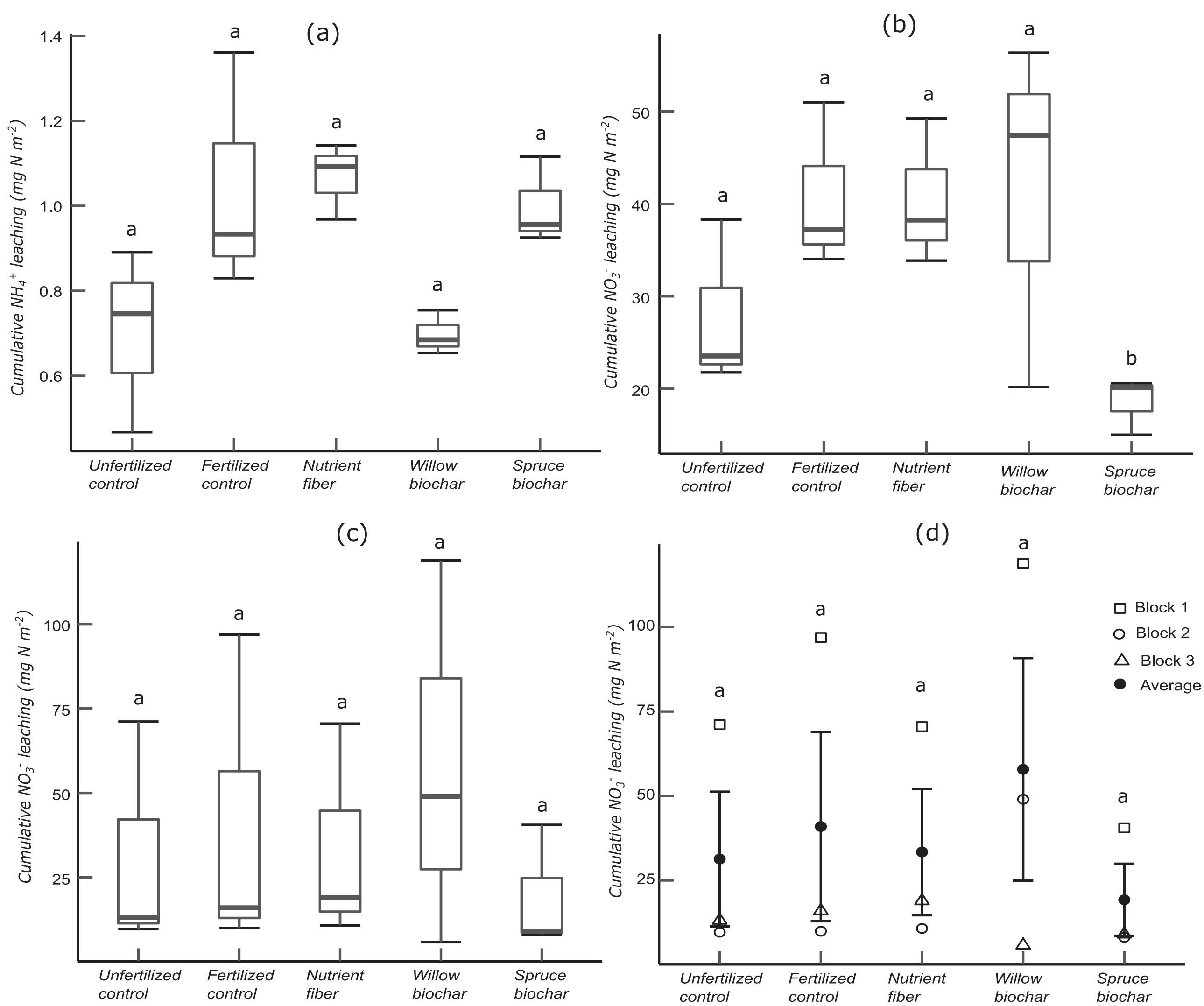

Fig. 2. a) Cumulative NH_4^+ leaching over the growing season, b) Cumulative NO_3^- leaching during the growing season, c) Cumulative NO_3^- leaching during the winter plant-free period, d) The NO_3^- leaching during the winter differed between the blocks. Treatments that differ statistically significantly ($p < 0.05$) from the fertilized control are marked with different lower case letters.

measurement period, the NO_3^- leaching dropped sharply, suggesting that growing plants took up the leachable NO_3^-. Usually, N leaching is negatively correlated with plant N uptake (Lemola et al., 2000; Moir et al., 2012). The 68% reduction in NO_3^- leaching in the spruce biochar treatment compared to the fertilized control over the growing season was significantly larger than the average reduction of 13% in biochar treatments found in a meta-analysis (Borchard et al., 2019). The winter data was more variable, and the differences between treatments were less clear than during the growing season. The larger variability in the N-leaching in winter compared to summer can be explained by a combination of occasionally very wet waterlogged conditions and freeze-thaw events, both of which occurred during our study period. These could affect the field unevenly due to spatial heterogeneity in inherent soil properties, such as soil compaction, which in turn affects water flow. In the meta-analysis by Gao et al. (2017), it was shown that freeze-thaw cycles can significantly increase soil NH_4^+ and NO_3^- concentrations, leaching of NO_3^- and dissolved organic N, as well as N_2O emissions. Disruption of soil aggregates during freeze-thaw cycles can also release N, and significantly decrease soil total N and MBN concentrations (Gao et al., 2017). The winter was so rainy that occasionally water was standing on the experimental plots. In general, based on visual observations, block 3 was wetter than the other blocks, and more often waterlogged. Water flow through the soil in block 1 was generally faster than in blocks 2 and 3, which could explain the higher NO_3^- leaching rates into the resin bags in this block during winter. Based on visual observation at the time of inserting the resin bags into the soil on 27 October 2017, the especially wet plots were two plots of fertilized fiber treatment (in blocks 2 and 3), and the fertilized control plot in block 2. Especially wet plots based on a later observation (23 November 2018) were willow biochar (block 1), fertilized control (block 2), and spruce biochar and unfertilized control (both in block 3), but except for the willow biochar plot in block 1, these plots did not stand out from the data as having higher N leaching rates. This exceptionally wet plot with very high NO_3^- leaching increased the average and standard deviation of the willow biochar treatment (Fig. 2c). However, it is noteworthy that the treatment averages still decreased in the same order, showing that even in the very wet winter conditions, the spruce biochar seems to have had the ability to reduce NO_3^- leaching rates, and could probably help to mitigate N-leaching losses during warmer and wetter winters in a changing climate.

4.2. Percentage of added fertilizer N leached

The average NO_3^- leaching rate across all treatments; 0.7 kg NO_3^--N ha^{-1} yr^{-1}, is at the lower end of estimates of NO_3^- leaching from Finnish clay soils under cereal crops, e.g. 1–38 kg NO_3^--N ha^{-1} yr^{-1} (Jaakkola,

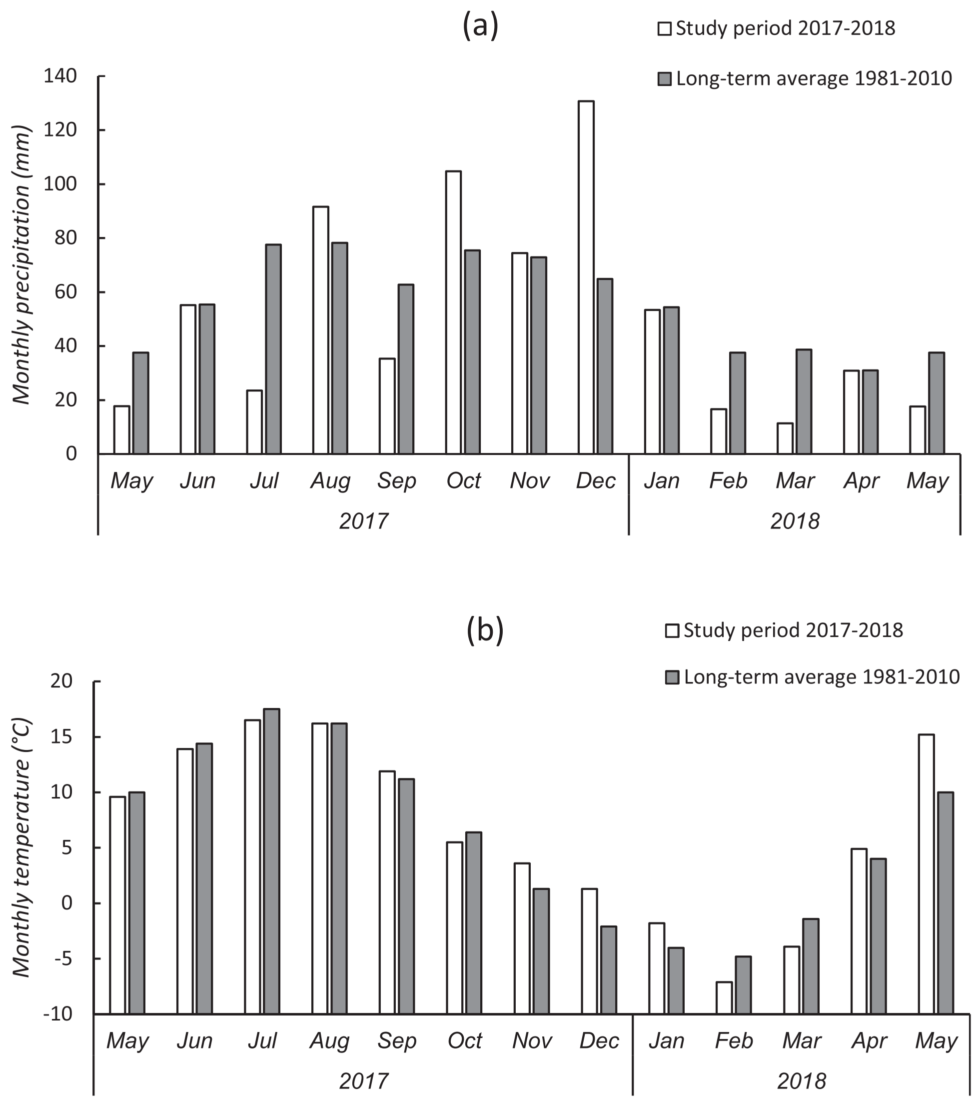

Fig. 3. Mean monthly precipitation (a) and temperature (b) during the study period along with the long-term average (1981–2010) recorded from meteorological station at Artukainen, Turku (FMI, 2020), which is about 30 km north-west from the experimental field.

Table 3
One-way blocked ANOVA results for the soil parameters.

Variable	Main effect	F	p
Soil NH_4^+ (mg N kg^{-1})	treatment	0.95	0.48
	block	0.68	0.54
Soil NO_3^- (mg N kg^{-1})	treatment	8.16	0.006*
	block	0.91	0.44
Soil MBC (mg C kg^{-1})	treatment	0.55	0.71
	block	1.16	0.36
Soil MBN (mg N kg^{-1})	treatment	0.73	0.60
	block	0.54	0.60

* $p<0.01$.

1984) or 2–22 kg N ha^{-1} yr^{-1} (Lemola et al., 2000) or 2–40 kg N ha^{-1} yr^{-1} (Salo and Turtola, 2006). The latter estimate also includes surface runoff. Also, these literature values are for fertilization rates of 90–100 kg N ha^{-1} yr^{-1}, and in our study the fertilization rate was even less (80 kg N ha^{-1} yr^{-1}). Even at these low fertilization rates, the spruce biochar could significantly reduce NO_3^- leaching. In the fertilized control treatment, on average 2.3% of the added NO_3^--N fertilizer was leached, while in the spruce biochar treatment only 1.1% was leached (Table 4). According to Jaakkola (1984), 1–4% of fertilizer-N used for cereals is lost when applied in the spring, and our values fall within this range.

4.3. Possible mechanisms of N retention in biochar amended soils

The smaller NO_3^- leaching rates in the spruce biochar treatment were supported by more NO_3^- retained in the surface soil, as seen also by Haider et al. (2017). There was a trend of lower NH_4^+ leaching from the willow biochar treatment, and on average higher retention of NH_4^+ in the topsoil of this treatment that also suggest a link between these two. The soil amended with willow biochar had the highest cation exchange capacity of all treatments (Table 1), which supports cation exchange as the mechanism of this elevated NH_4^+ retention. However, the cation exchange capacity of the soil in the willow biochar treatment was not statistically significantly higher than in the control treatment, which probably explains why the increase in NH_4^+ retention in this soil was not statistically significant either. The slight increase in the cation exchange capacity of the willow biochar amended soils implies that the willow biochar has cation exchange sites on its surfaces, but since this biochar had a low BET-surface area, the area of such reactive surface is limited. We speculate that the NO_3^- is retained physically inside the small biochar pores, as suggested by Kammann et al. (2015). This is supported by the higher BET-surface area and thus higher porosity in the spruce biochar that reduced NO_3^- leaching and increased soil NO_3^- retention in our

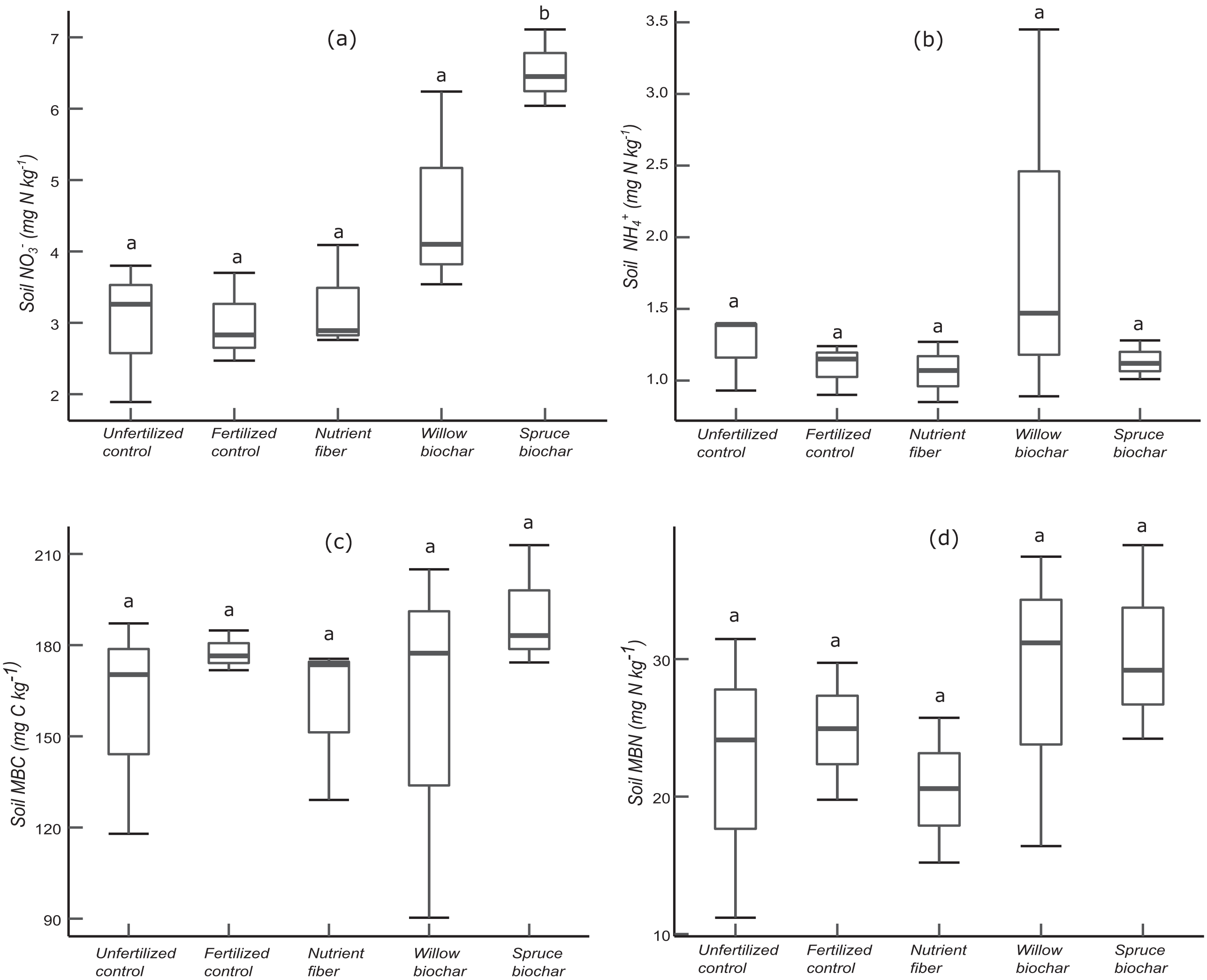

Fig. 4. a) Extractable soil NO_3^-, b) extractable NH_4^+, c) microbial biomass C and d) microbial biomass N in May 2018. Treatments that differ statistically significantly ($p < 0.05$) from the fertilized control are marked with different lower case letters.

experiment. The low BET-surface area and porosity of the willow biochar could explain why it did not reduce NO_3^- leaching. Heikkinen et al. (2019) found that the slow pyrolysis biochars were good in increasing water retention at field capacity, and we suggest that this improved water retention could also have helped to retain NO_3^- physically inside spruce biochar pores in our field study, as the internal porosity is known to directly affect soil water holding capacity (Rasa et al., 2018). Another reason why there might be more NO_3^- leaching from the willow biochar plots than from spruce biochar plots is the higher soluble N content of willow biochar (Table 2). However, the amounts of soluble N in either of the biochars - 0.1 kg N ha^{-1} (spruce biochar) or 0.31 kg N ha^{-1} (willow biochar) - are very small compared to the amount of N (80 kg N ha^{-1}) applied annually as NPK fertilizer. Also, the biochars were applied in the autumn 2016, and the N-leaching was measured during 2017–2018, so it is likely that most of the easily soluble N in the biochars itself would have leached away already during the autumn and winter of 2016. For these reasons, it is likely that the different effects of spruce and willow biochar on NO_3^- leaching were due to their inherent physical properties, rather than the N content of the biochar materials themselves. Key physical properties include the surface area and porosity, which affect NO_3^- retention inside the pores, as well as water flow through the biochar particles or biochar-soil aggregates.

The growing season cumulative N-leaching amounts were not related to wheat grain yield or grain N content. This could be due to the relatively small percentage of overall N leached. Another possibility is that the NO_3^- absorbed by biochar may not be easily available to plants (Haider et al., 2016; Joseph et al., 2018). While it has been known for some time that biochars can retain NH_4^+ through cation exchange (Hale et al., 2013; Wang et al., 2015), the finding that biochars can retain NO_3^- is rather new (Hagemann et al., 2017; Haider et al., 2016; Joseph et al., 2018). The capacity of biochars to retain both NH_4^+ and NO_3^- have been shown to increase with field aging (Hagemann et al., 2017; Haider et al., 2016; Mia et al., 2017), or co-composting (Kammann et al., 2015). Thus, it is interesting that in our study we could see a notable increase in NO_3^- retention and a reduction in NO_3^- leaching in the spruce biochar treatment already 1–2 years after biochar field application in a boreal climate, where the field aging process is expected to be slower than in warmer climates. This suggest that some fresh biochars could have NO_3^- retention capacity due to their inherent properties, or that the capacity develops shortly after field application also in boreal conditions. Turunen et al. (2020) have suggested that “mapping pore structure characteristics of biochars produced from a wide range of different feedstocks with different methods would benefit biochar design for a particular purpose”. We further suggest that combining such characterizations to NO_3^- retention measurements of each biochar type would be useful for development of tailored biochars that can retain NO_3^-. Such detailed mechanistic studies are necessary for understanding the role of the starting material and the manufacturing method in producing desirable biochar properties. Developing biochars that can retain NO_3^-, and thus reduce its leaching into waterways and potentially

Table 4
Grain yield and grain N content in the different treatments in 2017 (average ± standard deviation, n = 3), and the average annual cumulative NO_3^--N leaching given as % of total fertilizer N, and as % of fertilizer NO_3^--N applied in May 2017.

Treatment	Grain yield kg ha^{-1}	Grain N content mg N kg^{-1} d.w.	Annual NO_3^--N leached mg N m^{-2}	Fertilizer N leached % N	% NO_3^--N
Unfertilized control	3431 ± 547 b	24367 ± 4461 a	59.2 ± 43.5		
Fertilized control	4894 ± 232 a	28867 ± 3002 a	81.7 ± 46.8	1.0	2.3
Nutrient fiber	4413 ± 350 a	26100 ± 1229 a	73.9 ± 26.5	0.9	2.1
Willow biochar	4628 ± 94 a	30167 ± 929 a	99.2 ± 74.6	1.2	2.9
Spruce biochar	4784 ± 185 a	28533 ± 1779 a	37.8 ± 19.9	0.5	1.1

Different letters indicate statistically significant differences between treatments in the grain yield, or grain N content, compared to the Fertilized control treatment (Dunnett's test, 2-sided). Differences between treatments in NO_3^--N leaching were separately tested for the summer and winter cumulative leaching due to the different effect of the block factor depending on the season. Therefore statistical testing was not conducted for the annual cumulative NO_3^--N leached, presented in this table solely for the purpose of allowing comparison of the total leached amounts (as mg N m^{-2} or as % of added fertilizer N) to other previously published studies.

denitrification losses as N_2O, should be an important future research priority. We have recently shown that biochars that retain NO_3^- can also increase plant uptake of NO_3^-, and significantly reduce soil N_2O emissions (Kalu et al., 2021). This is important because globally the agriculture sector is responsible for 66% of gross anthropogenic N_2O emissions (Davidson and Kanter, 2014), and N_2O has 265 times higher 100-year global warming potential (GWP_{100}) than CO_2 (IPCC, 2013). Biochars could be a viable option for reducing NO_3^- leaching from agriculture, especially in catchments where reduction in N leaching from agricultural land would help to reduce eutrophication, such as in the coastal Baltic Sea area, where N leaching from agriculture significantly contributes to algal blooms (Savage et al., 2010).

We found no effect of soil amendments on soil MBC and MBN. The effects of biochar and other soil amendments on microbial biomass depend on the properties of these amendments. Biochars produced at low temperatures (< 300 °C) and from certain feedstock have higher contents of labile carbon, and have been previously found to increase soil microbial biomass (Cross and Sohi, 2011; Li et al., 2020). The biochars used in this study were produced from wood at a higher pyrolysis temperature (450 °C). According to the meta-analysis of Li et al. (2020), biochar produced from wood and at a higher pyrolysis temperature had no effect or only a minimal effect on soil microbial biomass. In addition, the labile carbon and nutrients in biochars may be available to microbes only for a short time after incorporation of soil amendments (Luo et al., 2011), and may have diminished already by the 2017–2018 field season. Another mechanism that could lead to increased microbial biomass in the biochar treatments are the favorable living habitats that the biochar pores and surfaces provide for soil microbes (Pietikäinen et al., 2000). However, that may not be enough to significantly increase the total microbial biomass of the soil either (Anders et al., 2013). There was a small tendency towards higher microbial N in the biochar treatments compared to the fertilized control, but the differences were not statistically significant, probably due to the abovementioned reasons. This suggests that the increased NO_3^- retention and decreased NO_3^- leaching in the spruce biochar treatment could be mainly explained via physical mechanisms.

We hypothesized that the nutrient fiber could enhance N retention in the soil through biological mechanisms. Previous studies show that incorporation of organic amendments with high C/N ratio, such as straw, can decrease NO_3^- leaching, because of reduced net soil N mineralization (Beaudoin et al., 2005), and mineral N immobilization into microbial biomass (Chantigny et al., 2013; Hartmann et al., 2014). However, we did not find support for a larger N storage in microbial biomass in the nutrient fiber treatment. Nutrient fiber is composed of mostly lignin. The addition of lignin may not significantly stimulate microbial activity because of its low decomposability and availability to the micro-organisms (Bahri et al., 2008; Schutter and Dick, 2001). Even though the C/N ratio of the nutrient fiber is not as high as that of the biochars, it is high enough to invoke microbial immobilization of N. The C/N ratio of nutrient fiber used here was 36, while 30 is considered as the limit value after which immobilization occurs (Alexander, 1977). However, as the added amount of nutrient fiber was rather low (3250 kg C ha^{-1}), it is likely that this one time application was not high enough to cause any longer term increase in microbial C and N that would still have been measurable in spring 2018. The application amount was chosen based on practical knowledge, so that the addition would not cause nitrate depression and reduction of plant growth and agronomic value, which has been observed to occur at higher application amounts. Also, as for biochars, it is likely that the most soluble and easily decomposable part of the nutrient fiber would have already been decomposed in 2016. The nutrient fiber addition did not significantly increase soil C concentrations compared to the fertilized control (Table 1). Since increases in microbial biomass usually correlate with increases in total C, and especially with increases in labile C amounts and availability in soil (Fang et al., 2020), a longer time-span and annual additions of nutrient fiber as soil organic amendment would probably be required to obtain a significant increase in soil microbial biomass and total soil C.

5. Conclusions

Our study shows that the potential reduction in NO_3^- leaching obtainable by the appropriate type of biochar soil amendments can be of considerable magnitude, even under boreal field conditions, and with realistic biochar field application rates (21 tons ha^{-1}). However, this increased N retention in soil, and reduced N leaching, may not necessarily lead to increased grain yields. This topic warrants more research to optimize the biochar manufacturing process in order to produce biochars that efficiently retain NO_3^- in a form that is available for plants, but safe from leaching.

CRediT authorship contribution statement

EV was responsible for the maintenance of the organic amendment field experiment. KK and BK planned the N leaching measurements. KK, AS and EV took care of the insertion and replacement of the resin bags in the field. BK organized the mineral N measurements from the resin bags, and BK and KK calculated the N-leaching results. SK conducted the microbial biomass and soil extractable mineral N measurements, and calculated the results. KK wrote the first manuscript draft, prepared figures and tables and conducted the statistics. SK and KK prepared the revised version of the manuscript, and SK made additional tables, statistical analysis, and prepared final versions of the figures. All co-authors commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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